

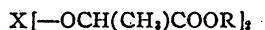
Diesters of Lactic Acid. Esterification of Lactates with Dibasic Acids

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Twenty-six esters made by the esterification of lactate esters with dibasic acids are described. Boiling points, refractive indices, densities and viscosities of the esters at different temperatures are given. Potential usefulness of these compounds as plasticizers is suggested.

In the previous paper of this series,² the adipates of a number of esters of lactic acid were described, and their potential usefulness as plasticizers was suggested.

The present paper reports work of the same general nature in which instead of adipic acid, various other dibasic acids were used to esterify the hydroxyl group of esters of lactic acid. These products may be represented by the formula



where X is the divalent acyl radical of a dibasic acid and R is the alcohol radical of the lactic ester. The dibasic acids used were phthalic, maleic, succinic, sebacic, carbonic and benzenephosphonic. Most attention was devoted to phthalic esters because of their importance in the plasticizer industry.

The products obtained by the esterification of dicarboxylic acids with allyl lactate contain two allyl groups in the molecule and are polymerizable. Several such esters have been reported. Thus, allyl lactate has been treated with acid chlorides to produce the carbonate, succinate, fumarate, adipate, sebacate and phthalate.³ The maleates of allyl⁴

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Rehberg and Dixon, *THIS JOURNAL*, **72**, 5757 (1950).

(3) Howald and Jones, U. S. Patent 2,462,042, Feb. 15, 1949.

(4) Jones, U. S. Patent 2,443,915, June 22, 1948.

TABLE I

PROPERTIES AND ANALYSES OF DIESTERS OF LACTIC ACID

Components of diesters Acid Lactate		Yield, %	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	n_D^{20}	n_D^{40}	d_4^{20}	d_4^{40}	Viscosity, cpds. 20° 40°	
Phthalic	Methyl ^a	78	56.8 56.6	5.4 5.4	1.4949	1.4875	1.2242	1.2074	7,495	459
Phthalic	Ethyl ^b	84	59.1 58.7	6.1 6.3	1.4870	1.4796	1.1715	1.1536	934	127.1
Phthalic	Butyl	61	62.5 62.4	1.4820	1.4748	1.1094	1.0924	283	69.0
Phthalic	2-Ethylbutyl	87	65.2 65.0	8.0 8.0	1.4838	1.4757	1.0878	1.0724	882	165.4
Phthalic	<i>n</i> -Octyl	82	67.4 67.1	8.7 8.9	1.4772	1.4700	1.0381	1.0248	250	64.9
Phthalic	2-Ethylhexyl	86	67.4 67.5	8.7 8.7	1.4790	1.4720	1.0423	1.0278	474	105.8
Phthalic	Allyl	80	61.5 61.6	5.7 6.0	1.4998	1.4922	1.1693	1.1529	351	75.2
Phthalic	2-Ethoxyethyl	75	58.1 57.6	6.6 6.6	1.4859	1.4788	1.1622	1.1446	725	118
Phthalic	2-Butoxyethyl	60	61.2 61.1	7.5 7.6	1.4802	1.4733	1.1092	1.0920	338	74.2
Phthalic	2-(2-Butoxy-ethoxy)-ethyl	96	60.2 59.9	7.8 7.9	1.4790	1.4722	1.1130	1.0966	298	77.8
Phthalic	Tetrahydrofurfuryl	90	60.2 59.8	6.3 6.6	1.5030	1.4978	1.2188	1.2037	31,640	2009
Maleic	Ethyl ^c	72	53.2 53.8	6.4 6.5	1.4462	1.4382	1.1244	1.1066	22.88	9.23
Maleic	Butyl	84	58.1 57.8	7.6 7.7	1.4488	1.4410	1.0852	1.0677	74.3	19.36
Maleic	Isobutyl ^d	83	58.1 57.6	7.6 7.1	1.4475	1.4396	1.0847	1.0678	189.5	42.9
Maleic	2-Ethylhexyl ^e	72	64.4 65.0	9.2 9.2	1.4564	1.4475	1.0134	0.9982	110.4	33.0
Maleic	Allyl ^f	46	56.5 56.2	5.9 5.9	1.4652	1.4561	1.1562	1.1382		
Succinic	Methyl	65	49.7 49.9	6.3 6.4	1.4408	1.4338	1.1925	1.1730	140.6	29.9
Succinic	Ethyl	78	52.8 52.6	7.0 6.7	1.4375	1.4305	1.1344	1.1138	54.0	16.94
Succinic	Butyl	87	57.7 57.9	8.1 8.2	1.4400	1.4330	1.0714	1.0529	44.7	16.52
Succinic	<i>n</i> -Octyl	98	64.2 64.2	9.5 9.8	1.4460	1.4394	1.0042	0.9878	56.8	21.1
Succinic	Allyl	92	56.1 56.6	6.5 6.7	1.4554	1.4472	1.1353	1.1170	48.9	16.9
Sebacic	Ethyl	76	59.7 59.4	8.5 8.8	1.4452	1.4382	1.0549	1.0370	58.3	22.6
Sebacic	Butyl	84	62.9 63.0	9.2 9.3	1.4465	1.4397	1.0200	1.0033	48.7	20.1
Sebacic	<i>n</i> -Octyl	81	67.3 68.0	10.2 10.4	1.4506	1.4438	0.9872	0.9626	63.0	26.9
Sebacic	2-Octyl	93	67.3 67.2	10.2 10.4	1.4475	1.4402	.9740	.9586	90.9	35.4
Carbonic	Allyl	83	54.5 54.4	6.3 6.6	1.4468	1.4392	1.1284	1.1089	26.3	10.9
Benzenephosphonic	Butyl ^g	25	58.0 57.8	7.5 7.5	1.4786		1.1082		52.7	

^a M.p. 50–55°. ^b M.p. 55–60°. ^c B.p. 62° (0.02 mm.). ^d B.p. 105° (0.02 mm.). ^e B.p. 150° (0.03 mm.). ^f B.p. 112° (0.02 mm.). ^g B.p. 130° (0.02 mm.).

and butyl^h lactates have been made with maleic acid or anhydride. The succinate of ethyl lactate has been made from potassium succinate and ethyl α -chloropropionate⁶ and from succinyl chloride and ethyl lactate.⁷

Table I shows the esters included in the present study. All the maleates, as well as the phthalates 2-ethylbutyl and 2-ethylhexyl lactates, were made by use of the acid anhydride. All other esters were made by use of the acid chlorides. The use of the dibasic acid or anhydride instead of the acid chloride resulted in the production of a mixture of esters instead of a single compound. However, in the cases studied, this mixture was as efficient a plasticizer for polyvinyl chloride as was the pure compound.⁸

Boiling Points.—Boiling points over a range of pressures were determined for most of the esters. Figures 1 and 2 are Cox charts showing $1/(t + 223)$, where t is the boiling point in °C., plotted versus $\log P$ (mm.).

A linear relationship was observed between the

(5) Carruthers and Blair, U. S. Patent 2,260,295, Oct. 28, 1941; cf. also Canadian Patent 411,766, April 13, 1943.

(6) Wurtz and Friedel, *Ann. chim.*, [3] **63**, 101 (1861).

(7) Wislicenus, *Ann.*, **133**, 257 (1865).

(8) Rehberg and Dixon, "Plasticizers from Lactic Acid. Direct Esterification of Butyl Lactate with Adipic Acid." Presented before the Division of Paint, Varnish and Plastics Chemistry, 116th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1949. See Abstracts of Papers, p. 23N.

boiling points at 1 mm. of diesters with and without lactic acid groups in the molecule [e.g., dibutyl phthalate as compared to bis-(butyl lactate)-phthalate]. The equation of this relationship is

$$X = 0.64Y + 118$$

where X and Y are the boiling points, at 1 mm. pressure, of the esters with and without the lactic acid groups, respectively. Of the twelve pairs of esters for which data were available, the maximum deviation was 5°, and the average deviation was 2.5°. From this equation it can be seen that the increase in boiling point caused by the introduction of lactic acid into the compound varied inversely with the boiling point of the compound. For the esters studied, this increase varied from about 40 to 100°.

Relationships similar to those given above for boiling points exist also for the vapor pressures ($\log P$) of the esters at any fixed temperature.

The refractive index, density and viscosity of each ester were measured at 20 and 40° and are shown in Table I. The usefulness of a compound as a plasticizer is usually increased by a low viscosity and a low temperature-viscosity coefficient. From the viscosity data in Table I it can be seen that methyl groups, branched chains, and especially ring structures tend to contribute high viscosity and high viscosity-temperature coefficient to those compounds in which these structures are found.

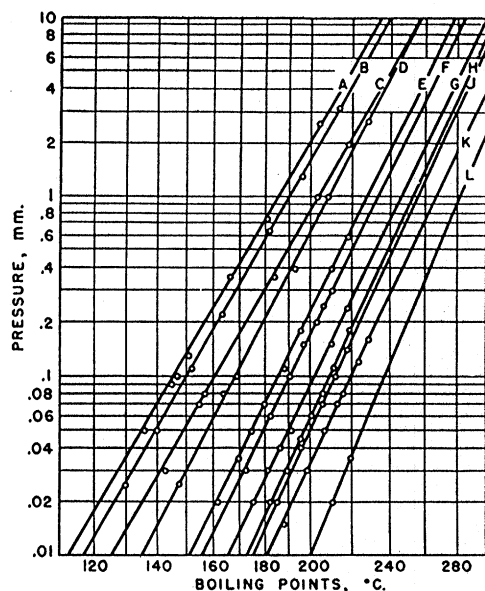


Fig. 1.—Boiling points of phthalates of various lactates: A, methyl; B, ethyl; C, allyl; D, butyl; E, 2-ethylbutyl; F, 2-ethoxyethyl; G, 2-ethylhexyl; H, 2-butoxyethyl; J, *n*-octyl; K, tetrahydrofurfuryl; L, 2-(2-butoxyethoxy)-ethyl.

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Experimental

Materials.—Those lactates not commercially available were made by the alcoholysis of methyl lactate.² The carbonate of allyl lactate was prepared by treating allyl lactate with α -carballyloxyethyl chloroformate (made from allyl lactate and phosgene by the Columbia Chemicals Division of the Pittsburgh Plate Glass Company and furnished to us through the courtesy of Dr. Franklin Strain). Benzene-phosphonyl chloride (benzenephosphorus oxydichloride) was kindly furnished by Dr. A. D. F. Toy, of the Victor Chemical Co.

Procedure.—Most of the compounds were made by the reaction of equivalent amounts of the acid chloride and the

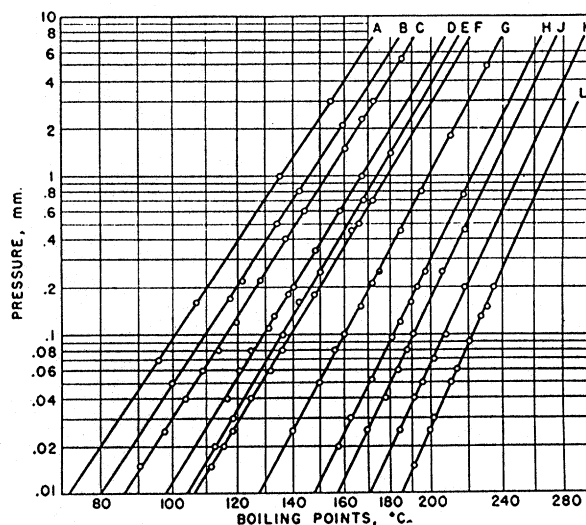


Fig. 2.—Boiling points of dicarboxylic acid esters of various lactates: A, allyl lactate carbonate; B, methyl lactate succinate; C, ethyl lactate succinate; D, allyl lactate succinate; E, butyl lactate maleate; F, butyllactate succinate; G, ethyl lactate sebacate; H, butyl lactate sebacate; J, *n*-octyl lactate succinate; K, 2-octyl lactate sebacate; L, *n*-octyl lactate sebacate.

lactate, in the presence of a slight excess of pyridine. The products were washed, dried and distilled. When the acid anhydrides were used, a 10 to 50% excess of lactate and a catalytic amount of sulfuric acid were used. The mixture was refluxed, vacuum being used as needed to keep the temperature below about 150°. Water was distilled out as fast as formed. When the reaction was complete, the catalyst was neutralized with sodium acetate and volatile materials were removed by vacuum distillation. Attempts to wash the crude products were often unsatisfactory because of the formation of emulsions.

All the products were distilled in an alembic type still specially designed for operation at low pressures.⁹ Boiling points at various pressures in the range 0.01–10.0 mm. were determined with the same still and used in the construction of Figs. 1 and 2.

(9) Ratchford and Rehberg, *Anal. Chem.*, **21**, 1417 (1949).